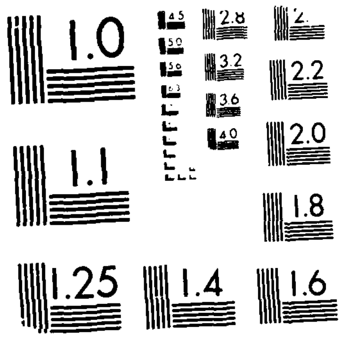
AD-A190 713 MAGNETIC ANOMALIES IN THE RARE EARTH OXIDE SUPERCONDUCTORS GDBA2CU3O(7-X) (U) NORTH CAROLINA UNIV AT CHAPEL HILL DEPT OF CHEMISTRY W E HATFIELD ET AL. 09 JAN 88 TR-3 N00014-76-C-0816 1/1

UNCLASSIFIED F/G 20/3 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

UNCLASSIFIED

DTIC FILE COPY (2)

AD-A190 713

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified	1b RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release Distribution Unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S)	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION Department of Chemistry University of North Carolina; 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION Office of Naval Research
6c ADDRESS (City, State, and ZIP Code) Chapel Hill, North Carolina 27514	7b ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217
8a NAME OF FUNDING/SPONSORING ORGANIZATION; 8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-76-C-0816
8c ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO; PROJECT NO.; TASK NO NR 053-617; WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification) UNCLASSIFIED: Magnetic Anomalies in the Rare Earth Oxide Superconductors $GdBa_2Cu_3O_{7-x}$ and $YbBa_2Cu_3O_{7-x}$

12 PERSONAL AUTHOR(S) William E. Hatfield, Brian R. Rohrs, Martin L. Kirk, Jeffrey H. Helms, Hyekyeong Ro, and Eric J. Williamson

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Technical Report	FROM ______ TO ______	January 9, 1988	12

16 SUPPLEMENTARY NOTATION

Technical Report No. 30

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	superconductivity, yttrium, barium, copper, ceramic oxide, perovskite, gadlinium, Meissner effect, spin-glass

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The magnetic properties of $GdBa_2Cu_3O_{7-x}$ and $YBa_2Cu_3O_{7-x}$ have been studied in low applied magnetic field by using pelletted sample. The magnetic behavior may be explained by the occurance of a spin-glass state due to a granular superconductor. The model assumes superconducting grains which are small compared to the penetration depth, and these are coupled into closed loops. Cooling in zero-field, followed by the application of a field at a fixed temperature produces a metastable state resulting in frustration and spin-glass behavior,

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a NAME OF RESPONSIBLE INDIVIDUAL William E. Hatfield	22b TELEPHONE (Include Area Code) 919-966-2297; 22c OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

88 1 12 170

OFFICE OF NAVAL RESEARCH

Contract N00014-86-K-0608

R&T Code 413a001-000-01

TECHNICAL REPORT NO. 30

Magnetic Anomalies in the Rare Earth Oxide Superconductors $GdBa_2Cu_3O_{7-x}$ and $YbBa_2Cu_3O_{7-x}$

by

William E. Hatfield, Brian R. Rohrs, Martin L. Kirk,
Jeffrey H. Helms, Hyekyeong Ro, and Eric J. Williamson

Department of Chemistry
The University of North Carolina
Chapel Hill, North Carolina 27599

Prepared for publication in
High Temperature Superconducting Materials; Preparations, Properties and Processing
William E. Hatfield and John H. Miller, Jr., Editors
New York: Marcel Dekker, Inc., 1988

Magnetic Anomalies in the Rare Earth Oxide Superconductors
$GdBa_2Cu_3O_{7-x}$ and $YbBa_2Cu_3O_{7-x}$

William E. Hatfield, Brian R. Rohrs, Martin L. Kirk, Jeffrey H. Helms,
Hyekyeong Ro, and Eric J. Williamsen

The University of North Carolina at Chapel Hill
Chapel Hill, North Carolina

The discovery of high T_c superconductivity in $YBa_2Cu_3O_{7-x}$[1,2] and this group's interest in the magnetic properties of rare earth compounds led to the study of paramagnetic analogs. Anomalous magnetic behavior in selected samples of two of these systems, $GdBa_2Cu_3O_{7-x}$ and $YbBa_2Cu_3O_{7-x}$ is reported here. A spin - glass like transition is present at temperatures below T_c. The glassy behavior in an annealed pellet of $GdBa_2Cu_3O_{7-x}$ is shown in Figure 1. The flat regions in the diamagnetic shielding curve show flux trapping upon reversing the temperature and cooling in a field, proof that the sample is still a superconductor. The anomalous behavior observed in the diamagnetic shielding shows a time decay over a period of two weeks (Fig. 2) resulting in an increasingly broadened transition. After three weeks, the same sample displays typical superconductor behavior, however, a small residual componant of the previous phase results in a slight decrease in the magnitude of the diamagnetic signal at 50 K. It is believed this transient glassy behavior is due to the sample being subjected to numerous thermal and magnetic cycles. The fact that subsequent samples lost this behavior after one series of such cycles confirms the metastability of this glassy state.

The Meissner signal for the sample showing the anomalous behavior and for the same sample after three weeks are essentially identical and show ~25% bulk diamagnetism. This is typical of a porous, granular superconducting composite.[3,4] The magnetic susceptibility of a powdered sample of $GdBa_2Cu_3O_{7-x}$ (Fig. 3) is qualitatively

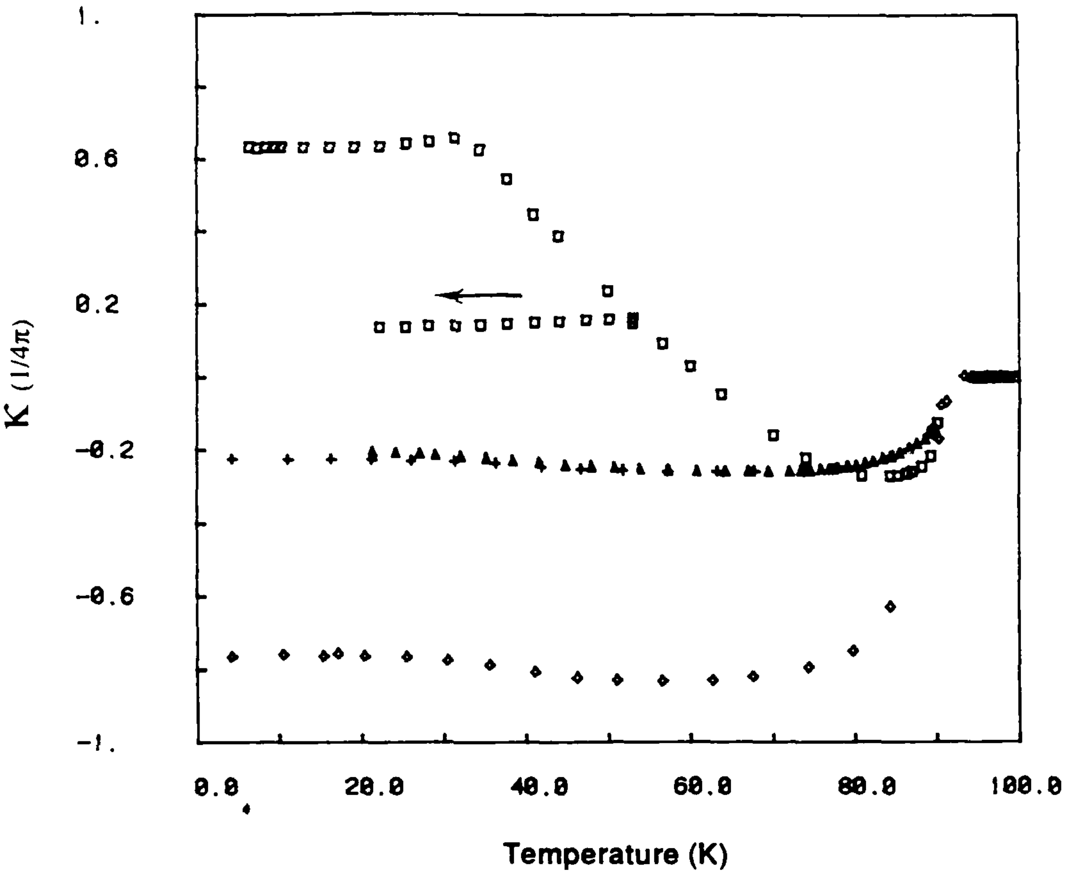


Figure 1. Volume susceptibility of $GdBa_2Cu_3O_{7-x}$ showing glassy behavior. Diamagnetic shielding (zero field cooled) signal of original sample □ , arrow demonstrates flux trapping upon cooling at 52°K. Meissner (field cooled) signal of original sample Δ . Diamagnetic shielding signal of same sample after three weeks ◊ showing ~85% total flux exclusion. Meissner signal after three weeks + . All susceptibilities are corrected for porosity and demagnetization effects.

similar to Figure 1, except that no increase in the susceptibility below T_c is seen. The fact that the diamagnetic shielding is less than the previous amount of 75% for the pellet may be due to the smaller particle size of the powder.

The $YbBa_2Cu_3O_{7-x}$ sample (Fig. 4) is very similar to $GdBa_2Cu_3O_{7-x}$ since it also shows the glass - like behavior. The Meissner signal is ~10% of the value for total flux exclusion. The magnetization of the $YbBa_2Cu_3O_{7-x}$ specimen (Fig. 5) is typical of a "dirty" superconductor. As the field increases, the magnetization is linear beyond H_{c1} and curves slowly due to the inability of flux to freely penetrate. Upon reversing the field, some of the flux is trapped at defect sites giving rise to the large hysteresis shown.

Several techniques have been used to determine sample purity. X-ray powder diffraction data give no evidence for a separate impurity phase. ICP-AES analysis yields an elemental stoichiometry of $Gd_1Ba_{1.922}Cu_{2.752}O_y$. Both of these techniques are accurate to within 5%. EPR spectroscopy (Fig. 6) at very high gain also yields none of the paramagnetic copper impurities witnessed by others.[5] However, a broad Gd signal is observed at high gain indicating the possibility of a minor impurity phase (less than 0.5%). Perhaps the most convincing evidence lies in the susceptibility measurements. The Meissner signals show none or very small amounts of the large glass-like signal. Furthermore, paramagnetic impurities that give signals of this magnitude do not suddenly

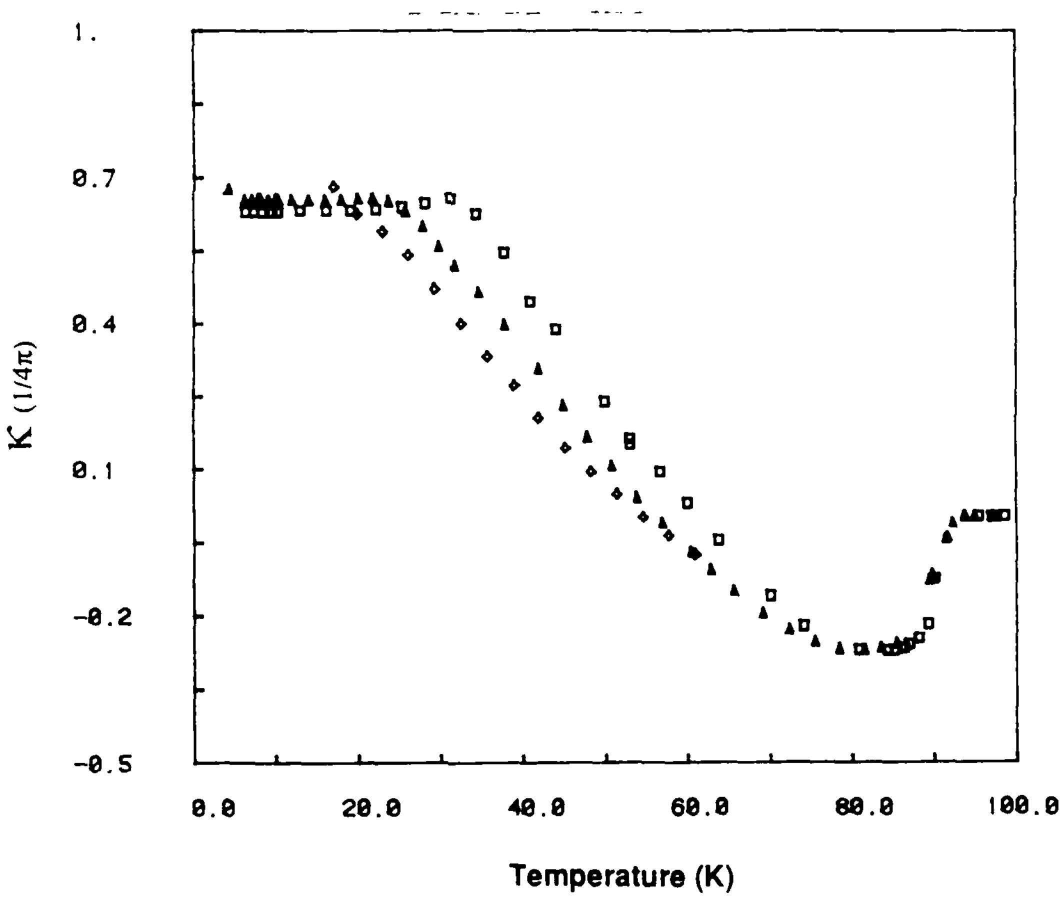


Figure 2. Diamagnetic shielding signal of $GdBa_2Cu_3O_{7-x}$ demonstrating signal decay over time: original sample □ , one day later Δ , after two weeks ◊ .

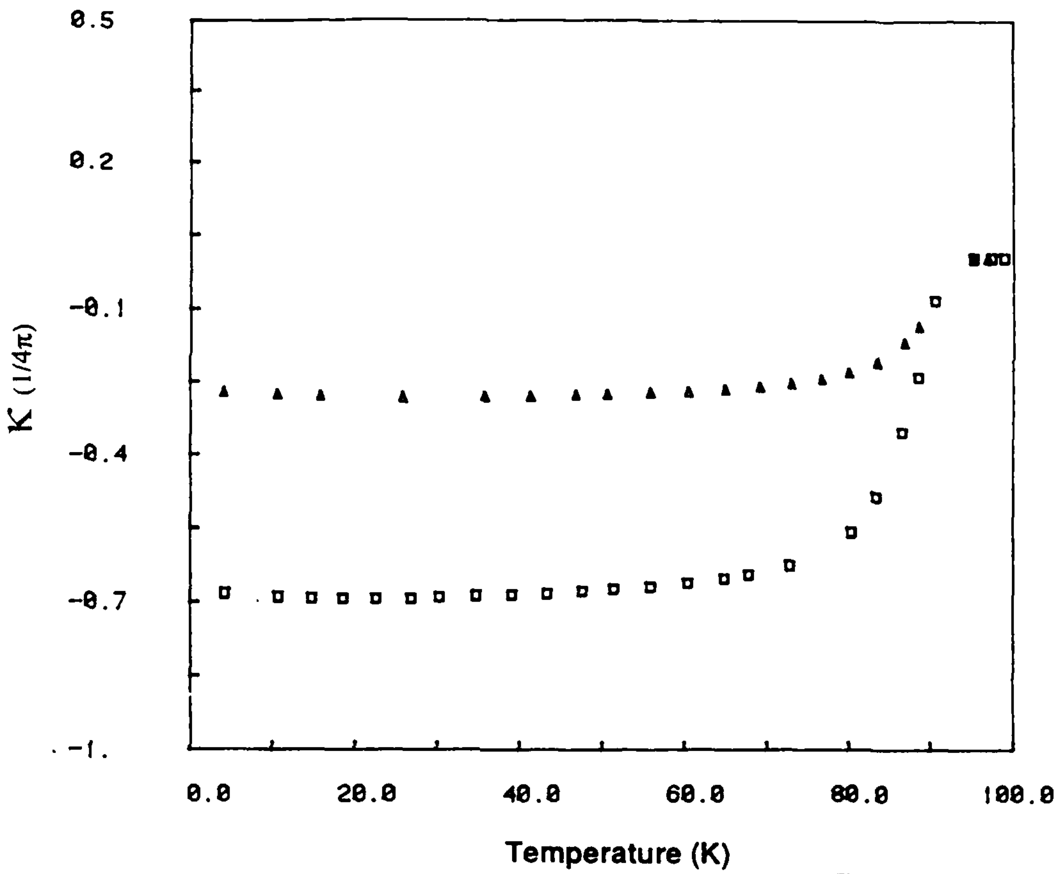


Figure 3. Volume susceptibility of a powdered sample of $GdBa_2Cu_3O_{7-x}$ showing typical superconductor behavior. The Meissner effect Δ is ~25% and the diamagnetic shielding □ is ~70% of perfect diamagnetism.

dissipate. It can be conclusively stated that the signal is caused by some other phenomenon.

One explanation for this behavior is the occurance of a spin-glass state due to a granular superconductor.[6,7] The basic model involves superconducting grains, each small compared to the penetration depth, which are weakly coupled into closed loops. At finite fields, these clusters are frustrated, i.e., they cannot find a state which minimizes all bond energies simultaneously. Consequently, there are numerous competing ground states with nearly equal energy. Cooling in zero-field, followed by the application of a field at a fixed temperature, produces a metastable state resulting in frustration and spin-

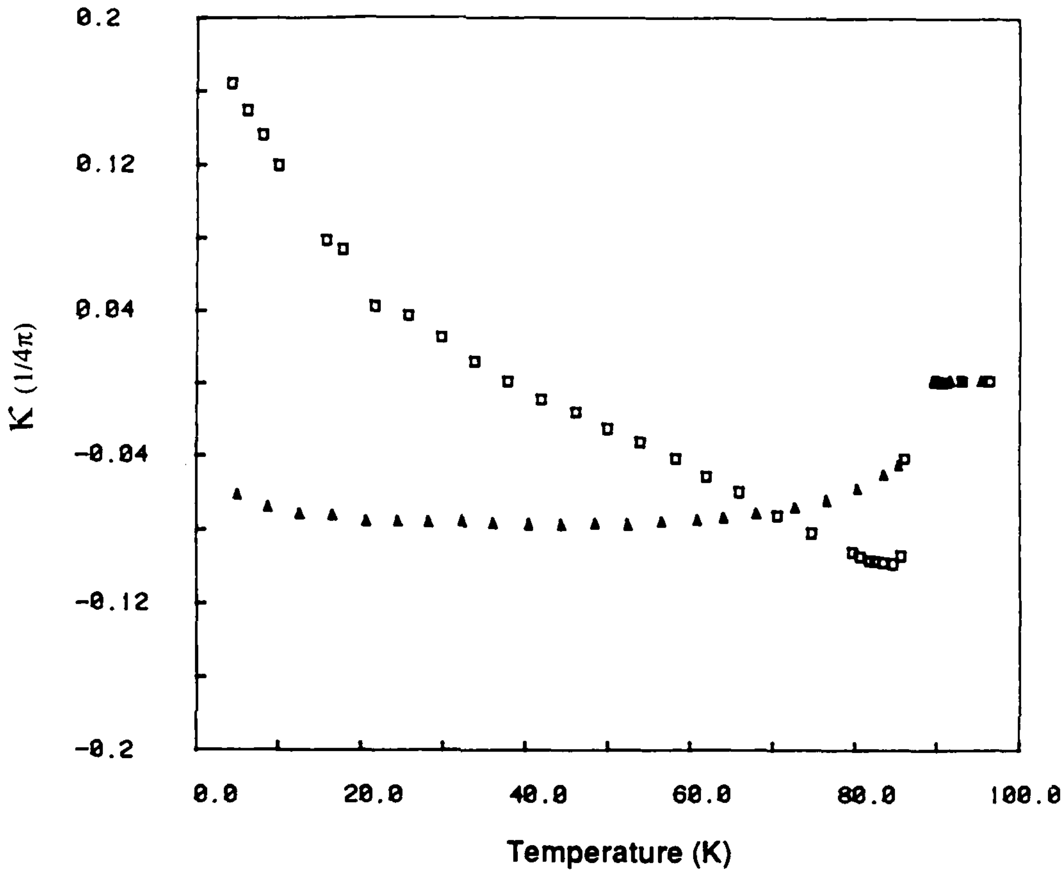


Figure 4. Volume susceptibility of $YbBa_2Cu_3O_{7-x}$. Diamagnetic shielding signal □ . Meissner signal Δ .

glass like behavior. If the sample is cooled slowly in a fixed field, the clusters are in equilibrium and a typical Meissner signal results.

This explanation, however, does not account for the large positive increase in the susceptibility. It accounts only for a decrease in the diamagnetism. Since X-ray powder diffraction and ICP-AES provide evidence that the impurities are less than 5%, small Gd impurities may form mictomagnetic clusters resulting in spin-glass formation.[8,9] The ZFC curve is a result of these clusters being frozen at some temperature $T<T_c$ in a frustrated manner. Upon warming, the rigid glass softens and the magnetic clusters relax. Thermal disorder then causes a time averaged magnetization which manifests itself in a decrease

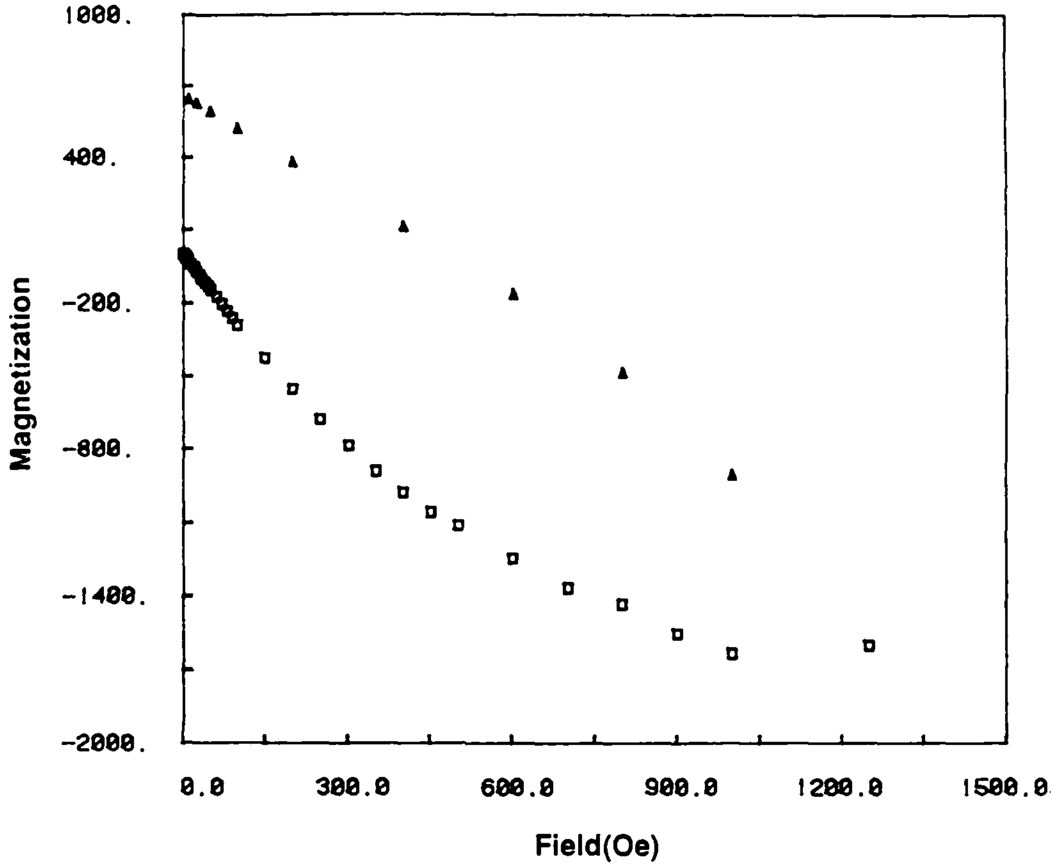
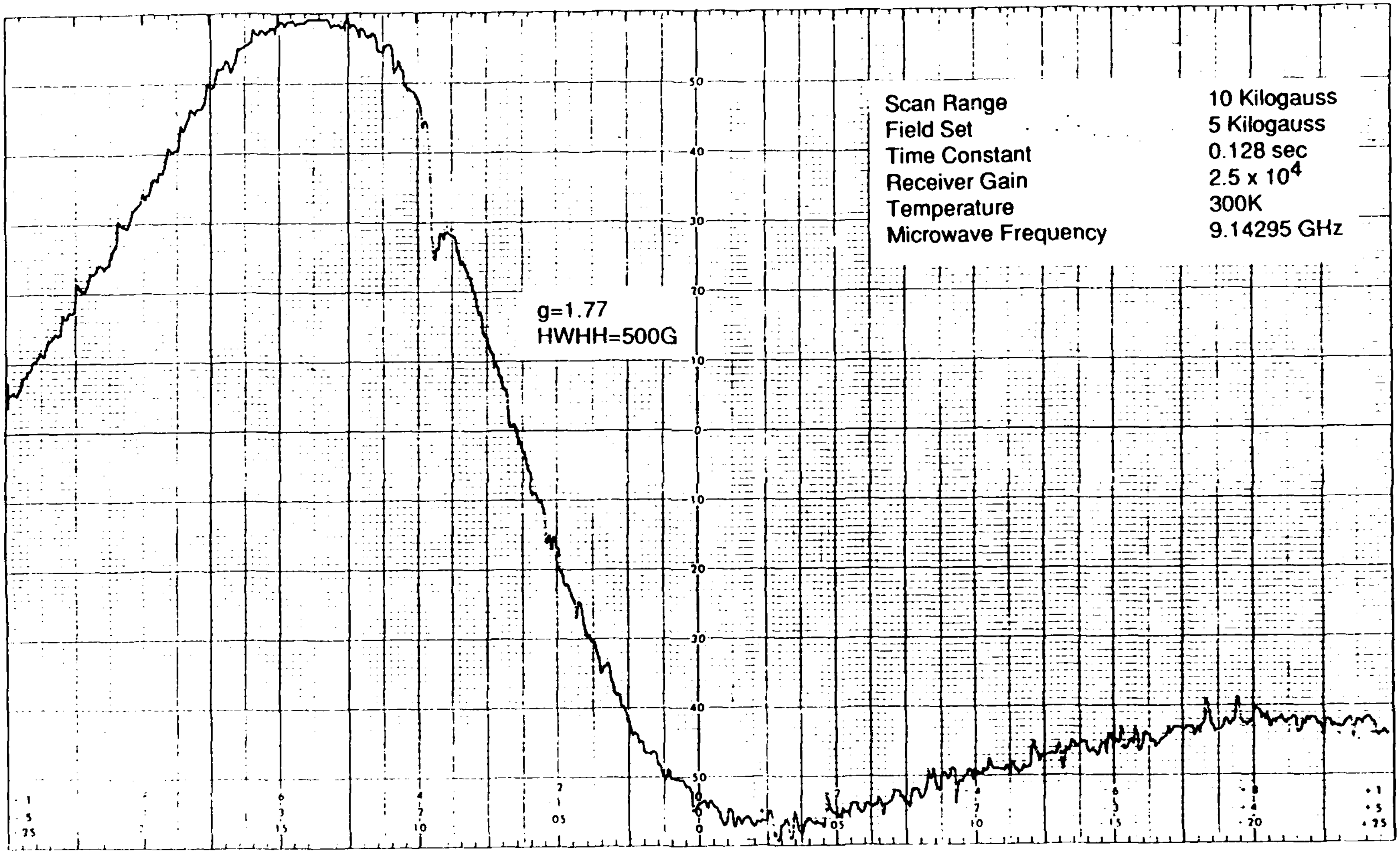


Figure 5. Magnetization of $YbBa_2Cu_3O_{7-x}$ showing hysteresis due to flux trapping. Increasing field □ , decreasing field Δ .

Figure 6. (Next page) Room temperature X-band EPR signal of $GdBa_2Cu_3O_{7-x}$ showing no copper impurities and a small Gd^{2+} signal. The small absorption at g =2.00 is from a DPPH standard. The Gd^{2+} signal is not due to Gd_2O_3 which has g ≈1.86 and HWHH ≈330G.

in the susceptibility. In the FC curve, the temperature is gradually decreased and the cluster spins have time to minimize their energy, resulting in no net contribution to the magnetization by the impurity ions. Thermal and magnetic cycling may tend to break up these domain-like clusters. This may explain the transient nature of the observed glassy behavior.



Scan Range 10 Kilogauss
Field Set 5 Kilogauss
Time Constant 0.128 sec
Receiver Gain 2.5 x 10^4
Temperature 300K
Microwave Frequency 9.14295 GHz
g=1.77
HWHH=500G

ACKNOWLEDGEMENT

This work was supported in part by the Office of Naval Research.

REFERENCES

1. C.W. Chu, preprint

2. M.K. Wu, J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang, and C.W. Chu, *Phys. Rev. Lett.*, *16*, 908 (1987).

3. Y. Yeshurun, I. Felner, and H. Sompolinsky, *Phys. Rev. B, 36,* 840 (1987).

4. J.M. Tarascon, W.R. McKinnon, L.H. Greene, G.W. Hull, and E.M. Vogel, *Phys. Rev. B, 36,* 226 (1987).

5. R. Jones, M.F. Ashby, A.M. Campbell, P.P. Edwards, M.R. Harrison, A.D. Hibbs, D.A. Jefferson, A.I. Kirkland, T. Thanyasiri, and E. Sinn, "Synthesis, Chemistry, Electronic Properties ans Magnetism in the Y-Ba-Cu-O Superconductor Systems", In "Chemistry of High-Temperature Superconductors", D.L. Nelson, M.S. Whittingham, and T.F. George, Eds., ACS Symposium Series 351, p. A1, 1987.

6. C. Ebner, and D. Stroud, *Phys. Rev. B, 31,* 165 (1985).

7. S.John, and T.C. Lubensky, *Phys. Rev. Lett., 55,* 1014 (1985).

8. P.J. Ford, *Contemp. Phys., 23,* 141 (1982).

9. D. Davidov, K. Baberschke, J.A. Mydosh, and G.J. Nieuwenhuys, *J. Phys. F, 7,* L49 (1977).

DL/413/83/01
053/413-2

ABSTRACTS DISTRIBUTION LIST, 053

Dr. M. F. Hawthorne
Department of Chemistry
University of California
Los Angeles, California 90024

Professor O. T. Beachley
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. W. Hatfield
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Professor R. Wells
Department of Chemistry
Duke University
Durham, North Carolina 27706

Professor K. Neidenzu
Department of Chemistry
University of Kentucky
Lexington, Kentucky 40506

Dr. J. Zuckerman
Department of Chemistry
University of Oklahoma
Norman, Oklahoma 73019

Professor R. Neilson
Department of Chemistry
Texas Christian University
Fort Worth, Texas 76129

Professor M. Newcomb
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Professor L. Miller
Department of Chemistry
University of Minnesota
Minneapolis, Minnesota 55455

Professor K. O. Christe
Rockwell International
Canoga Park, California 91304

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies		No. Copies
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1	Naval Weapons Center Attn: Dr. A. B. Amster Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1		

END
DATE
FILMED
4-88
DTIC